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(21)Application number : 11-010006 (71)Applicant : SUMITOMO ELECTRIC IND LTD

(22)Date of filing : 19.01.1999 (72)Inventor : HARADA KEIZO

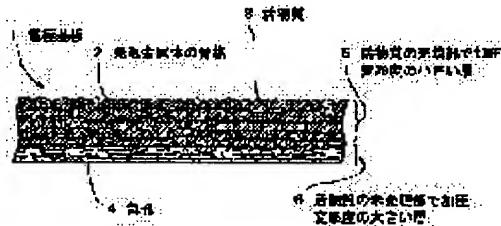
 MATSUI YASUYUKI  
 YAMANAKA SEISAKU

## (54) BATTERY ELECTRODE SUBSTRATE AND MANUFACTURE THEREOF

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a low-cost battery electrode substrate without using two kinds or more of materials, capable of sufficiently carrying a required active material and of intensively carrying collected electricity with low resistance.

SOLUTION: In this battery electrode substrate 1 filled with an active material 3 in a foam metal body, one side in the thickness direction of the foam metal body is filled with the active material 3, layer A 5 with a smaller compressed deformation. On the other side thereof is not filled with the active material 3, layer B 6 with a greater compressed deformation. Thereby, a double-layered structure is formed with the layer A 5 for collecting electricity and the layer B 6 for carrying the electricity with a smaller internal electrical resistance loss so that a charge collecting effect is great and charging and discharging of a large current is possible.



## LEGAL STATUS

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CLAIMS

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[Claim(s)]

[Claim 1] One side of the thickness direction of the foam-metal object which is the electrode substrate for cells with which the active material was filled up into the foam-metal object, and was produced by Mr. \*\*\*\* 1 is an electrode substrate for cells characterized by having two-layer structure after filling up with the active material, the degree of pressurization deformation being small, the side else having the large degree of pressurization deformation, without filling up with an active material and the metal frame of the foam-metal object having continued.

[Claim 2] The electrode substrate for cells according to claim 1 characterized by being the composition whose aforementioned active material the aforementioned foam-metal object makes nickel a subject, and makes nickel hydroxide a subject.

[Claim 3] The electrode substrate for cells according to claim 1 characterized by the skeleton of the aforementioned foam-metal object being the composition to which the inside of a skeleton is covered with double structure, the outside of iron and a skeleton is covered with nickel or cobalt, and the aforementioned active material considers nickel hydroxide, cobalt, or the powder of a cobalt compound as a subject.

[Claim 4] The manufacture method of the electrode substrate for cells characterized by suspending restoration operation before filling up with an active material the foam-metal object produced by Mr. \*\*\*\* 1 from one side of the thickness direction and filling up total thickness, and pressurizing the foam-metal object in the thickness direction after that.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the electrode substrate for cells used for the rechargeable battery which is used for portable electronic equipment, an electric vehicle, etc., and in which charge and discharge are possible. [0002] [Description of the Prior Art] Although there is a \*\*\*\* cell in the rechargeable battery in which charge and discharge are possible as a dc-battery for automobiles in ancient times, recently, the rechargeable battery of high electric capacity with lightweight nickel-cadmium battery, nickel hydride battery, lithium cell, etc. is developed, and it is mainly used for portable electronic equipment. Such a rechargeable battery uses a metal for the electrode substrate, and although the electrical and electric equipment is accumulated between the active material supported by it and the counter electrode through separator, the amount of charges and discharges is decided by the amount of an active material, and distance between plates. Then, the method of supporting the active material of many in the limited space, and contracting the distance of an electrode substrate and a counter electrode is adopted by using a metal porous body for an electrode substrate, stuffing an active material into a porous body, or piling up an electrode substrate, separator, and a counter electrode in the shape of a sheet.

[0003] The material range is decided by the active material for which the metal of an electrode substrate used here is used. Usually, nickel is used in a nickel-cadmium battery or a nickel hydride battery, and many aluminum is used in the lithium cell now. In case the chemical reaction by the charge and discharge of a cell ionizes an active material or returns this to non-ion, it is for being corroded by ion, or an electrode substrate's serving as a metal ion, and preventing the obstacle and bird clapper of a cell performance.

[0004] And the configuration of the metal of an electrode substrate is so good that the capacity which receives adhesion with an active material and can support an active material is large. What also depends a metal porous body on sintering of a metal powder although a metal porous body came to be used from there cannot take large porosity, therefore the rate of support of an active material is a low. Moreover, although it is also possible to obtain big porosity and it can take the large rate of support of an active material by the size of the fiber which the thing using a metal fiber as a nonwoven fabric uses, since the adhesion of metal fibers is based on the contact between fiber, it is disadvantageous as an electrode skeleton which is the role which collects the electrical and electric equipment generated in the active material. After what is used well now makes an urethane foam etc. a skeleton and carries out electric conduction-ized processing to this, its foam-metal object acquired by carrying out metallic coating by plating and removing pitches, such as an urethane foam, with a roasting furnace after that is in use. In addition, after carrying out electric conduction-ized processing to the nonwoven fabric of a resin, metallic coating is carried out by plating and the metal nonwoven fabric which removes a resin with a roasting furnace is also used.

[0005] although active materials, such as nickel hydroxide, are made into the shape of a paste, and are inserted in a sheet-like metal plate and it is filled up with an active material into pore when using such a metal porous body as an electrode substrate, the adhesion of pressurizing after restoration and making it predetermined thickness, simultaneously an active material and a metal skeleton is raised. Although an active material is ionizing whenever it repeats charge and discharge, or returning to non-ion and incorporates or emits ion when it becomes a cell, a metal porous body carries out supply of ion, and the role of recovery as the path. Therefore, the structure where the metal skeleton has entered like a vessel between active materials is desirable, and, as for the metal skeleton, moreover, it is ideal as a charge collector to give a thicker path in the direction connected with the electrode of a cell.

[0006] One of the device of the is indicated by the Japanese Patent Publication No. No. 27823 [ 63 to ] official report, and it shows the content to drawing 3 . After making the letter resin 21 of foaming, and the porous fibrous resin 22 into one and carrying out metallic coating to this, by carrying out calcining of the resin and removing it, produce the metal porous body of two-layer structure, a foaming metal layer is made to support an active material, and a fibrous metal layer is an electrode substrate which considers the role of reinforcement as a charge collector. When such structure is used as a cell, an active material will gather for an electrode through the metal skeleton of a fibrous metal layer, and the electrical and electric equipment by which the foaming metal layer which supports an active material entered even into the details of a metal skeleton, and was collected has it. [ convenient ]

[0007] Moreover, in the Provisional-Publication-No. No. 140359 [ 62 to ] official report, as shown in drawing 4 , one side is indicating the electrode substrate which are the foaming metal 23 of high porosity, and the foaming metal 24 of low porosity [ sides / other ], and filled this up with the active material with the foaming metal of the continuous three-dimensions mesh pattern. The foaming metal whose other sides this one side is high porosity and are low porosity plates by arranging an anode only in one side to usually plating by arranging an anode to both sides of the urethane foam which applied carbon, it lessens the amount of plating of an opposite side mostly (low porosity) (high porosity), and the amount of plating of the side which has arranged the anode is manufactured. By turning the field of the foaming metal 23 of high porosity up, being filled up with an active material, and maintaining this posture to dryness and a pressurization process, the purpose does not omit an active material and tends to raise the pack density.

[0008]

[Problem(s) to be Solved by the Invention] The electrode substrate of two-layer structure given in the Japanese Patent Publication No. No. 27823 [ 63 to ] official report is very difficult in respect of the stability of quality on manufacture. That is, there is quality variation in the letter resin of foaming used as a material and other porous fibrous resins, the distribution of fiber is not stabilized like a resin foam by the porous fibrous resin, but it is easy to generate roughness and fineness partially. Moreover, when it goes electric conduction-ized processing to these together, it is difficult to be necessarily unable to perform electric conduction-ized processing uniformly, but to also set like the

galvanizer of a subsequent metal, and to obtain uniform plating processing from the difference between the kind of resin material used as a frame, the size of a frame, etc.

[0009] Moreover, although the electrode substrate which are the foaming metal of high porosity [ one side / of a Provisional-Publication- No. No. 140359 / 62 to / official report ] and the foaming metal of low porosity / sides / other ] is good invention, manufacture takes a long time and becoming cost quantity is not avoided. namely, plating which arranges an anode only on one side -- it is -- a lot of plating to the field -- attaching -- and -- on the other hand -- being also alike -- in order to attach plating of requirements -- delivery of a low speed -- not plating -- it is because it does not obtain but productivity becomes low

[0010] Then, this invention offers the electrode substrate which can concentrate and pass the electrical and electric equipment which could fully support the necessary active material and collected the current by low resistance by the low cost.

[0011]

[Means for Solving the Problem] Not using two or more kinds of materials, this invention offers the electrode substrate of two-layer structure, after the metal frame has continued from the single foam-metal object. That is, it is the electrode substrate which comes to fill up a foam-metal object an active material, and one side of the foam-metal object produced by Mr. \*\*\*\* 1 is filled up with an active material, and the small layer which is the degree of pressurization deformation, and the side else are electrode substrates for cells to which the degree of pressurization deformation is characterized by the bird clapper from a large layer, without filling up with an active material. Although what made nickel the subject is desirable as for the foam-metal object used here, otherwise, aluminum, gold, silver, copper, platinum, molybdenum, manganese, cobalt, and titanium are sufficient as it. And as for an active material, what becomes the composition which makes nickel hydroxide a subject is desirable.

[0012] Moreover, a foam-metal object is double structure and iron and the thing by which the outside of a frame is covered with nickel or cobalt also have [ the frame of the metal ] the inside of a frame desirable [ an object ]. And that from which an active material becomes the composition which makes a subject nickel hydroxide, cobalt, or the powder of a cobalt compound also obtains a good result.

[0013] Before the manufacture method of an electrode substrate is uniformly filled up with active materials, such as nickel hydroxide, from one side of a foam-metal object and all of the thickness directions of the foam-metal object are filled up with it, it suspends restoration operation, and after dryness, by pressurizing in the thickness direction, one side of a foam-metal object is filled up with an active material, and it manufactures the side else as a state where it is still non-filling. After the foam-metal object used here electric-conduction-ization-processes a resin foam, it is desirable in it being what is obtained by carrying out nickel plating, and is acquired by the same method also in aluminum, gold, silver, copper, platinum, molybdenum, manganese, cobalt, and titanium. Moreover, the foam-metal object of the double structure acquired by plating nickel or cobalt on the foam-metal object of an application, baking, and the obtained steel frame rank that carried out calcining in the paste which makes a subject iron powder or iron oxide powder at a resin foam is also desirable.

[0014] Thus, the electrode substrate of the two-layer structure which consists of an active material packed bed and a non-filling layer after the produced metal frame has continued has very little fracture of the metal frame of an active material non-filling layer, even when radial is pressurized when rolling an electrode substrate spirally and manufacturing a cylindrical cell and it manufactures a square shape cell, after winding spirally. In order to hardly apply tensile stress to a metal frame with flexibility since there is no existence of an active material even if it bends in the metal frame of an active material non-filling layer and external force is added to what bending stress and tensile stress are applied to a metal frame by existence of an active material, and a metal frame tends to fracture if this is bent in the metal frame of an active material packed bed and external force is added, a metal frame is because it is hard to fracture. Thus, since the current collection frame of an active material packed bed and the frame of an active material non-filling layer which passes the electrical and electric equipment are the foam-metal objects of one, the electrode substrate of the two-layer structure which it comes to produce can manufacture easily the thing of the quality of conformance which excelled [ loss / internal electric resistance ] in the performance as a cell few, and was stabilized in the low cost.

[0015]

[Embodiments of the Invention] The cross section which the electrode substrate 1 of the two-layer structure by which pressurization deformation was carried out expanded to drawing 1 in the thickness direction of this invention is shown. The foam-metal object of a drawing top is filled up with the active material 3, and the degree of pressurization deformation of the skeleton 2 of a foam-metal object is small A horizon 5. And a lower foam-metal object is not filled up with an active material 3, but the degree of pressurization deformation of the skeleton 2 of a foam-metal object is large B horizon 6.

[0016] The electrical and electric equipment generated from A horizon 5 with which the active material 3 of this plate is filled up gets across to B horizon 6 which exists where pore is crushed through the skeleton 2 of a foam-metal object, and gets across to the electrode (not shown) of a cell. B horizon 6 with which this active material is not filled up is only a \*\*\*\* metal, and since there is little fracture of the skeleton 2 of the foam-metal object at the time of a press, elevation of electric resistance is suppressed. That is, since it has two-layer structure of A horizon 5 which collects the electrical and electric equipment, and B horizon 6 with few internal electric resistance losses which pass the electrical and electric equipment, the current collection effect is large and the charge and discharge of a high current of it become possible.

[0017] An example of the manufacturing process is shown in drawing 2. The foam-metal object 7 to prepare applies carbon powder to a resin foam, and has the method which plates by performing electric conduction-ized processing, and the method of making a metal powder or metallic-oxide powder the shape of a paste as an option at a resin foam, and plating after an application, dryness, and calcining. The foam-metal object 7 of a tabular is placed horizontally, and with water soluble resins (carboxymethyl cellulose etc.) and water, nickel hydroxide or nickel hydroxide, and cobalt powder are made into the shape of a paste, and are inserted in this from the top. That is, the amount of pastes which fills up with Mr. Fukashi predetermined with the pump 8 of a constant pressure the active material 3 made into the shape of a paste into the pore 4 of the foam-metal object 7 sent in the direction of an arrow at a fixed speed, and fills it up with it per area of the foam-metal object 7 is controlled, and the restoration of an active material 3 to foam-metal object thickness is adjusted.

[0018] It pressurizes in the thickness direction of a foam-metal object after drying this, and is made predetermined thickness. Consequently, the metal frame portion which forms the foaming space near the globular form with which the active material is filled up is pushed in the thickness direction, and becomes an ellipse spherical. And the metal frame portion with which the active material is not filled up loses \*\*\*\* space, becomes flat, and is crushed in the shape of a metal plate.

[0019] Since the electrode substrate of this two-layer structure has A horizon 5 which the quality on manufacture is also stabilized, and it can manufacture easily by the low cost, and fills up with an active material, and collects the electrical and electric equipment, and B horizon 6 made of the foam metal of one which passes the electrical and electric equipment, it becomes what has a few internal electric

resistance loss. That is, in the electrical and electric equipment which the active material entered even into the details of a metal skeleton, and collected there, through B horizon 6 of other near shape of a flat metal plate, A horizon 5 which supports an active material will gather for an electrode, and the electric discharge of a high current of it is attained.

[0020] (Example 1) nickel -- \*\*\*\* with a thickness [ of a subject ] of 3.0mm -- the foam-metal object produced uniformly was sent at a fixed speed, the active material of the shape of a paste which made nickel hydroxide the subject was stenciled, putting a fixed pressure on it with a pump, and thickness of 1.4mm and a non-filling portion was set to 1.6mm for the thickness of a packing fraction This was pressurized so that it might become the thickness of 0.7mm, and as for one side, the active material obtained the electrode substrate which it fills up and has the shape of a metal plate with the non-filling side else. This was judged to 35mm long and 75mm wide, and the lead board was attached by spot welding.

[0021] It wound spirally through this nickel pole, a MmNi (misch-metal nickel) system hydrogen storing metal alloy pole well-known as a partner pole, and the polypropylene nonwoven fabric separator that performed hydrophilic processing among these both, and the electrode substrate group was constituted, this was inserted in the sheathing can, the sheathing can was sealed with the obturation board after pouring in the electrolytic solution, and the cylindrical nickel hydride battery was obtained. This is set to No.1B. In addition, the lithium hydroxide of 30 g/l was added and used for the electrolytic solution at the causticity potassium solution of specific gravity 1.3.

[0022] (Example 2) The skeleton of a foam-metal object inserted the paste-like active material in the foam-metal object with a thickness of 3.0mm by which the inside of a skeleton was covered with double structure and the outside of iron and a skeleton was covered with nickel, and set thickness of 1.4mm and a non-filling portion to 1.6mm for the thickness of a packing fraction. This was pressurized so that it might become the thickness of 0.7mm, and as for one side, the active material obtained the electrode substrate which it fills up and has the shape of a metal plate with the non-filling side else. This was judged to 35mm long and 75mm wide, and the lead board was attached by spot welding. And the cylindrical nickel hydride battery was obtained in the same procedure as an example 1 using this electrode substrate. Let this be No.2B.

[0023] As an example of comparison, after nickel pressurized the foam-metal object with a thickness [ of a subject ] of 3.0mm at the thickness of 1.4mm, total thickness was covered, the paste-like active material was stenciled, and this was pressurized so that it might become the thickness of 0.7mm. The cylindrical nickel hydride battery of the example of comparison was obtained like the example using this electrode substrate. This is set to No.3B. And the discharge voltage and capacity in the case of the discharge currents 1A, 5A, and 10A of three kinds of cells of No.1 B-No.3B were investigated. A result is shown in Table 1.

[0024]

[Table 1]

電池No.	1 A放電		5 A放電		10 A放電	
	V	m A h	V	m A h	V	m A h
1 B(実施例1)	1. 21	980	1. 08	930	0. 97	875
2 B(実施例2)	1. 21	980	1. 08	925	0. 96	870
3 B(比較例)	1. 20	970	1. 03	880	0. 91	800

[0025] It is a solution or \*\* that capacity (mAh) is improving sharply as it becomes high current electric discharge from this result by cell No.1B of an example and 2B compared with cell No.3B of the example of comparison. Moreover, similarly, compared with cell No.3B of the example of comparison, by cell No.1B of an example, and 2B, discharge voltage (V) is improving as it becomes high current electric discharge. This is because it became possible to lower the internal electric resistance loss of an electrode substrate by flowing to an electrode through the layer by which pressurization deformation of the current collection from the layer with which the active material is filled up, and its electrical and electric equipment is carried out, without filling up with an active material.

[0026] Next, the foam-metal object with which thickness differs was filled up with the active material of a constant rate per area. The ratio of the layer which exists where the layer and pore with which the active material is filled up by this are crushed is changeable. That is, the foam-metal object which made the subject thickness 2.0 and 3.0 or 4.0mm nickel is prepared, an active material is stenciled like an example, and the thickness of a packed bed was made to be respectively set to 1.4mm. These were compressed into the thickness of 0.7mm. The electrode substrate which changed the ratio of the layer which exists where the layer and pore with which the active material is filled up are crushed by this was manufactured. These three kinds of electrode substrates are shown in Table 2.

[0027]

[Table 2]

プレス前の厚み (mm)		プレス後の厚み (mm)	
全厚み	充填部厚み	未充填部厚み	全厚み
2. 0	1. 4	0. 6	0. 7
3. 0	1. 4	1. 6	0. 7
4. 0	1. 4	2. 6	0. 7

[0028] Using three kinds of electrode substrates of Table 2, a cylindrical nickel hydride battery is manufactured in the same procedure as an example, and the result which investigated the discharge voltage and capacity at the time of electric discharge of 1A, 5A, and 10A is shown in Table 3.

[0029]

[Table 3]

プレス前の 全厚み(mm)	1 A放電		5 A放電		10 A放電	
	V	mAh	V	mAh	V	mAh
2.0	1.21	980	1.06	910	0.94	850
3.0	1.21	980	1.08	930	0.97	875
4.0	1.21	980	1.11	945	0.99	900

[0030] Consequently, if a non-filling layer becomes large and the internal electric resistance loss of an electrode substrate becomes small, in voltage (V) and capacity (mAh), the electric discharge property of a high current rose, and the effect of a fall of internal electric resistance has shown up. By changing the thickness of a metal porous body according to the discharge current from these, the electrode substrate according to the required amount of current can be obtained.

[0031]

[Effect of the Invention] Since two-layer structure is made to the electrode substrate of this invention by the method of restoration of the foam-metal object made by one of an active material, the metal frame is continuing and its current collection performance is good. Therefore, generation of heat by internal electric resistance can be suppressed, and the electrode substrate which can carry out the charge and discharge of the big power can be obtained by the low cost.

[Translation done.]